

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT SPECIFICATION

(11) 1 509 739

1 509 739

- (21) Application No. 40560/75 (22) Filed 3 Oct. 1975
 (31) Convention Application No. 2 447 727
 (32) Filed 7 Oct. 1974 in
 (33) Fed. Rep. of Germany (DE)
 (44) Complete Specification published 4 May 1978
 (51) INT CL³ C08K 5/53; C08L 77/00
 (52) Index at acceptance

C3R 22C 22D1A2 22D1AX 22D1B2 22D1BX 22D2A2
 22D2AX 22D2B2 22D2BX 22D3B 22D3D1 22N1B
 C12 C13M C13P C14A C22 C23 C24 C28X C29
 C33A C33B C5B1 C6AX C6X L1B L2C1 L4A
 L4C L6F



(54) FLAME RETARDING POLYAMIDE COMPOSITIONS

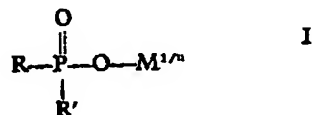
(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame retarding polyamide compositions.

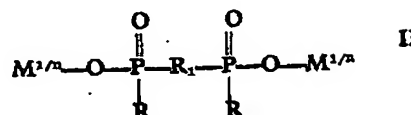
It is known that red phosphorus and organo-phosphorus compounds may influence the flammability of polyamides, and that in certain cases they have a good flame retarding effect.

The difficulty of using organo-phosphorus compounds for flameproofing polyamides resides in the fact that these compounds often have insufficient stability under the manufacturing or processing conditions necessary for polyamides, that they are not chemically inert in certain cases, or that they have a too high vapor pressure and thus volatilize when thermal stress is put on the polyamide, especially at reduced pressure.

The present invention provides a polyamide composition comprising a polyamide and as flameproofing agent, from 6 to 40 weight %, calculated on the polyamide, of a salt of a phosphinic acid of the formula



or a diphosphinic acid of the formula



in which

M is an alkali metal or a metal of the second or third group of the Periodic System,

n is the valency of the metal M,

each of R and R' is an alkyl or cycloalkyl radical having from 1 to 16, preferably from 1 to 6, carbon atoms, or an aryl or aralkyl radical having from 6 to 16 carbon atoms, and

R₁ is an alkylene, cycloalkylene, arylalkylene, arylene, arylene-alkylene or arene-bisalkylene radical having from 1 to 6, preferably from 2 to 4, carbon atoms in the alkylene radical.

Suitable organo-phosphorus compounds for use according to the present invention are for example the alkali, alkaline earth, magnesium, zinc and aluminium salts of dimethyl phosphinic, methylethylphosphinic, methylpropylphosphinic, methylhexylphosphinic, ethylphenylphosphinic, diethylphosphinic, ethane-1,2-dimethylphosphinic, ethane-1,2-diethylphosphinic, ethane-1,2-diphenylphosphinic and butane-1,4-dimethylphosphinic acids.

Especially preferred compositions of the salts of phosphinic and diphosphinic acids of the formulae I and II. The amount of phosphinic or diphosphinic salt depends on the polyamide and the flameproofing requirements, and is from 6 to 40, preferably from 8 to 30, weight %, calculated on the weight of the polyamide.

The polyamides which, in combination with the metal salts of the phosphinic acids of formulae I and II, yield the compositions of the present invention, are especially amorphous

polyamides which are derived for example, from such main diamine components as 1,3- or 1,4-bis-(aminomethyl)-cyclohexane, 2,5- or 2,6-bis-(aminomethyl)-bicyclo[2,2,1]heptane, dimethyl-bis-(4-aminocyclohexyl)-methane, 2,2,4- or 2,4,4-trimethylhexamethylene-diamine or xylylene-diamine.

The polyamides are derived for example, from

- 10 (i) from 5 to 50 mol %, preferably from 10 to 35 mol %, of 1,3-bis-(aminomethyl)-cyclohexane and/or 1,4-bis-(aminomethyl)-cyclohexane and/or 2,5-bis-(aminomethyl)-bicyclo[2,2,1]heptane and/or 2,6-bis-(aminomethyl)-bicyclo[2,2,1]heptane and/or at least one bis-(4-aminocyclohexyl)-derivative of an alkane having from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms, and/or *m*-xylylene-diamine, or a mixture of *m*-xylylene-diamine with up to 50 mol %, preferably up to 30 mol % of *p*-xylylene-diamine;
- 15 (ii) from 0 to 45 mol %, preferably from 0 to 35 mol %, of at least one straight-chain or branched aliphatic diamine having from 4 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, the amino groups being separated by at least 4 carbon atoms, preferably by at least 6 carbon atoms;
- 20 (iii) from 5 to 50 mol %, preferably from 10 to 35 mol %, of at least one aromatic dicarboxylic acid having from 7 to 20 carbon atoms, preferably from 8 to 14 carbon atoms, especially a mononuclear aromatic *m*- or *p*-dicarboxylic acid;
- 25 (iv) from 0 to 45 mol %, preferably from 0 to 35 mol %, of at least one saturated, straight-chain or branched aliphatic dicarboxylic acid having from 6 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, the carboxyl groups being separated by at least 4 carbon atoms; and
- 30 (v) from 0 to 80 mol %, preferably from 0 to 50 mol %, of at least one aliphatic amino-carboxylic acid having from 2 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, especially an ω -amino-carboxylic acid, or its lactam, the mol % sum of components (i) and (ii) equalling the mol % sum of components (iii) and (iv), the mol % sum of all components (i), (ii), (iii), (iv) and (v) being 100,
- 35 the mol % sum of components (i) and (iii) being from 20 to 95, preferably 50 to 90,
- 40 the mol % sum of components (ii), (iv) and (v) being from 5 to 80, preferably from 10 to 50, and
- 45 all the mol percentages being calculated on the sum of all components (i), (ii), (iii), (iv) and (v).
- 50
- 55
- 60

The polyamides used in the compositions of the present invention may be prepared according to known processes. Diamine(s), dicarboxylic acid(s) and optionally aminocarboxylic acid(s) or its/their lactam(s) are introduced the addition of water. It is often convenient to prepare first a salt based on the starting components, this salt then being introduced into the steel autoclave, optionally with water. The contents of the autoclave are heated to from approximately 200 to 260°C while stirring. Steam is then discharged and the temperature increased to from 265 to 300°C. At this temperature condensation is continued in a nitrogen current, optionally under reduced pressure, until the polyamide has attained the desired molecular weight.

Polyamides with especially high molecular weights and good mechanical properties are obtained by submitting the polyamides prepared in the autoclave to condensation in a further processing step, preferably in a double screw extruder under reduced pressure.

The polyamides should have a reduced specific viscosity (RSV) — determined on a solution of 1 g of polyamide in 100 ml of a 60:40 by weight mixture of phenol/tetrachloroethane at 25°C — of from 0.7 dl/g to 3.0 dl/g, preferably from 0.9 to 2.8 dl/g.

The phosphinic acid salts of the formulae I and II may be added to the starting polycondensation batch, or to the finished polyamide, or at any time during the polycondensation. When adding the phosphinic acid salts to a finished polyamide, they are advantageously mixed with the granulated polyamide, and this mixture is either processed directly, for example on an injection moulding machine, or first melted in an extruder, granulated and then processed after drying.

The flame retarding action of the phosphinic acid salts is examined according to ASTM D 635—68 on test specimens having dimensions of 127 × 12.7 × 1.6 mm. The polyamide compositions of the present invention are either self-extinguishing or non-flammable, depending on the concentration of the flameproofing agent. For example, a content of 20 weight % of the zinc salt of dimethylphosphinic acid in a polyamide obtained from 0.9 mol of terephthalic acid, 0.1 mol of isophthalic acid, 1.02 mols of 1,3-bisaminomethyl-cyclohexane, and 30 weight % of adipic acid-hexamethylene-diamine salt ensures sufficient flame retarding properties.

The phosphorous compounds contained in the flame retarding polyamide compositions of the present invention are thermostable and do not adversely affect the polyamides either during their preparation or during their processing, and because of their salt characteristics, they are non-volatile under the preparation and processing conditions.

In addition to the phosphinic acid salts,

65

70

75

80

85

90

95

100

105

110

115

120

125

there may be added to the compositions of the present invention inorganic fiber materials in the usual amounts, for example glass fibers, and fibers of quartz, asbestos or carbon. The thickness, especially of the glass fibers, is advantageously from 0.1 to 50, preferably from 3 to 15, microns, and their length advantageously from 0.01 to 5, preferably from 0.05 to 1, mm. The amount of the fibers is advantageously up to 50, preferably from 10 to 30, weight %, relative to the compositions.

The polyamide compositions of the present invention may also contain further additives, for example stabilizers, lubricants, dyestuffs, mould release agents, antistatics and fillers.

The flameproofed polyamide compositions of the present invention are suitable for the manufacture of articles for engineering purposes, for example construction pieces for electrical automatic machines and structural members in apparatus, parts of mechanical transmission in data processing systems.

The following Examples illustrate the invention.

EXAMPLE 1a:

A mixture of 66.4 g of terephthalic acid, 32.4 g of a bisaminomethylnorbornane mixture, 49.8 g of ϵ -caprolactam and 37.2 g of the disodium salt of ethane-1,2-dimethylphosphinic acid was slowly heated to 275°C with agitation and under a nitrogen atmosphere. The water formed in the condensation was distilled off via a descending condenser. The reaction batch was maintained at 275°C for another hour, and subsequently, 178 g of solid polyamide were obtained.

The product cooled by dipping into liquid nitrogen was ground in a cross beater mill, dried for 5 hours under reduced pressure (less than 1 mm Hg) at 180°C, and compression molded at 235°C to plates having a thickness of 1.6 mm (RSV 1.34 dl/g). The test specimens (127 × 12.7 × 1.6 mm) obtained by sawing were subjected to the combustion test according to ASTM D 635—68. The result of the test is indicated in Table 1.

EXAMPLE 1b: (Comparative Example)

A polyamide of terephthalic acid, bisaminomethylnorbornane mixture and ϵ -caprolactam was prepared as described in Example 1a, but without addition of the phosphinic acid salt, and tested according to ASTM D 635—68 (Table 1).

In order to prepare the bis-(aminomethyl)-norbornane mixture, 2-cyano-bicyclo[2,2,1]heptane-5 was hydroformylated. The reaction mixture was reacted with ammonia and hydrogen to form the bis-(aminomethyl)-norbornane mixture.

EXAMPLE 2:

A mixture of 66.4 g of terephthalic acid,

58 g of 1,3-bis-aminomethyl-cyclohexane (mainly present in the trans-form), 36.3 g of ϵ -caprolactam and 32.9 g of disodium salt of ethane-1,2-dimethylphosphinic acid was slowly heated to 275°C under a nitrogen atmosphere and with agitation. The water formed in the condensation was distilled off via a descending cooler. The reaction batch was maintained at 275°C for a further hour, and 152 g of solid polyamide were then obtained.

Test specimens were manufactured from the product in the manner described in Example 1a (RSV 1.02 dl/g), and subjected to the combustion test according to ASTM D 635—68. The result of the test is indicated in Table 1.

EXAMPLE 3a:

A mixture of 149.5 g of terephthalic acid, 16.6 g of isophthalic acid, 145.1 g of 1,3-bis-aminomethyl-cyclohexane, 116.7 g of adipic acid-hexamethylene-diamine salt (AH salt) and 93 g of zinc salt of dimethylphosphinic acid was heated slowly to 275°C in a nitrogen atmosphere and with agitation. Polycondensation occurred, and the condensation water was distilled off via a descending cooler. The reaction batch was maintained at 275°C for a further hour. 391.5 g of solid polyamide having a milky white color were obtained.

According to the indications given in Example 1a, test specimens (RSV 0.98 dl/g) were manufactured and subjected to the combustion test according to ASTM D 635—68. The material was non-flammable, as indicated in Table 1.

EXAMPLE 3B: (Comparative Example)

A polyamide was prepared according to Example 3a from terephthalic acid, isophthalic acid, 1,3-bis-aminomethyl-cyclohexane and AH salt, but without addition of the phosphinic acid salt, and tested according to ASTM D 635—68 (Table 1).

EXAMPLE 4:

As described in Example 3a, a polyamide was prepared in which 93 g of zinc salt of dimethylphosphinic acid were replaced by 96 g of disodium salt of ethane-1,2-dimethylphosphinic acid. The product obtained with a yield of 420 g was non-flammable according to the combustion test of ASTM D 635—68, as indicated in Table 1. RSV of the test specimens: 0.88 dl/g.

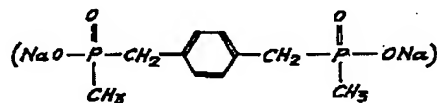
EXAMPLE 5:

As described in Example 3a, a polyamide was prepared in which the zinc salt of dimethylphosphinic acid was replaced by the same amount of the zinc salt of ethane-1,2-dimethylphosphinic acid. 420 g of product were obtained. RSV of the compression molded plate: 0.92 dl/g. The test according to

ASTM D 635—68 proved the non-flammability, as indicated in Table 1.

EXAMPLE 6:

- 5 As described in Example 3a, a polyamide was prepared in which the zinc salt of dimethylphosphinic acid was replaced by 90 g of disodium salt of *p*-xylylene-dimethylphosphinic acid of the formula



The product obtained with a yield of 416 g was non-flammable according to the ASTM D 635—68 test, as indicated in Table 1. RSV of the compression molded plate: 0.82 dl/g.

10

TABLE 1

Example	Starting components of the polyamido	Flameproofing agent (FPA)	Added FPA wt. %	Compression molded plate RSV (dl/g)	Result acc. to ASTM D 635-68
1a	TA, BN, ϵ -caprolactam	disodium salt of ethane-1,2-dimethylphosphinic acid	18.5	1.34	non-flammable
1b	TA, BN, ϵ -caprolactam	—	—	1.47	flammable
2	TA, 1,3-BAC, ϵ -caprolactam	disodium salt of ethane-1,2-dimethylphosphinic acid	18.5	1.02	non-flammable
3a	TA/IA, 1,3-BAC, AH salt	zinc salt of dimethylphosphinic acid	20.0	0.98	non-flammable
3b	TA/IA, 1,3-BAC AH salt	—	—	1.10	flammable
4	TA/IA, 1,3-BAC, AH salt	disodium salt of ethane-1,2-dimethylphosphinic acid	20.4	0.88	non-flammable
5	TA/IA, 1,3-BAC, AH salt	zinc salt of ethane-1,2-dimethylphosphonic acid	20.0	0.92	non-flammable
6	TA/IA, 1,3-BAC, AH salt	disodium salt of <i>p</i> -xylylene-dimethylphosphinic acid	20.0	0.82	non-flammable

TA = terephthalic acid;

IA = isophthalic acid;

BN = bisaminomethylnorbornane mixture;

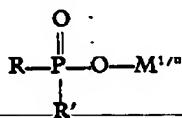
1,3-BAC = 1,3-bisaminomethylcyclohexane;

AH salt = adipic acid-hexamethylene diamine salt;

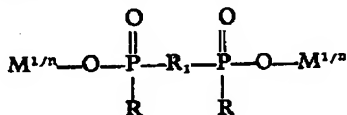
RSV = reduced specific viscosity, measured on solutions of 1 g. of polyamide in 100 ml of phenol/tetrachloroethane (60/40 weight %) at 25°C.

WHAT WE CLAIM IS:—

1. A polyamide composition comprising a polyamide and as flameproofing agent, from 6 to 40 weight %, calculated on the polyamide
 5 of a salt of a phosphinic acid of the formula



or a diphosphinic acid of the formula



in which

- 10 M is an alkali metal or a metal of the second or third group of the Periodic System,
 n is the valency of the metal M ,
 each of R and R' is an alkyl or cycloalkyl radical having from 1 to 16 carbon atoms, aryl
 15 or aralkyl radicals having from 6 to 16 carbon atoms, and
 R_1 is an alkylene, cycloalkylene, arylalkylene, arylene, arylene-alkylene or arene-bisalkylene radical having from 1 to 6 carbon atoms in
 20 the alkylene radical.

2. A composition as claimed in claim 1, which contains the phosphinic or diphosphinic acid salt in an amount of from 8 to 30 weight %, calculated on the polyamide.

3. A composition as claimed in claim 1 or claim 2, wherein the phosphinic or diphosphinic acid salt is a zinc salt.

4. A composition as claimed in any one of claims 1 to 3 wherein the polyamide is an amorphous polyamide derived from, as diamine component, 1,3- or 1,4-bis-(aminomethyl)-cyclohexane, 2,5- or 2,6-bis-(aminomethyl)-bicyclo[2,2,1]heptane, dimethyl-bis-(4-aminocyclohexyl)-methane, 2,2,4- or 2,4,4-trimethylhexamethylene-diamine or xylylene-diamine.

5. A composition as claimed in any one of claims 1 to 4, which also contains a filler.

6. A polyamide composition as claimed in claim 1 substantially as described in any one of Examples 1 to 6 herein.

7. A shaped article comprising a polyamide composition as claimed in any one of claims 1 to 6.

ABEL & IMRAY,
 Chartered Patent Agents,
 Northumberland House,
 303—306 High Holborn,
 London WC1V 7LH.